Interactions between organic additives and active powders in water-based lithium iron phosphate electrode slurries

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HIGHLIGHTS

► We clarify interactions between the water-based organic additives and $LiFePO_4$.
► $LiFePO_4$ prefers to interact with SBR than with SCMC.
► The conductive agents prefer to interact with SCMC than with SBR.
► To enhance electrochemical performance, a sequenced adding process is suggested.

GRAPHICAL ABSTRACT
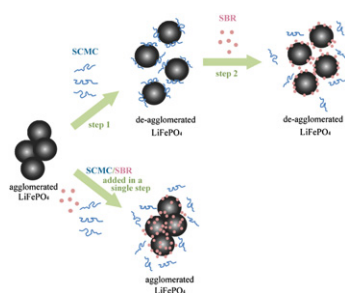
ABSTRACT

The interactions of organic additives with active powders are investigated and are found to have great influence on the determination of the mixing process for preparing electrode slurries with good dispersion and electrochemical properties of lithium iron phosphate ($LiFePO_4$) electrodes. Based on the analyses of zeta potential, sedimentation, and rheology, it is shown that $LiFePO_4$ prefers to interact with styrene—butadiene rubber (SBR) relative to other organic additives such as sodium carboxymethyl cellulose (SCMC), and thus shows preferential adsorption by SBR, whereas SBR has much lower efficiency than SCMC in dispersing $LiFePO_4$. Therefore, for SCMC to interact with and disperse $LiFePO_4$ before the interaction of $LiFePO_4$ with SBR, it is suggested to mix SCMC with $LiFePO_4$ prior to the addition of SBR during the slurry preparation process. For the electrode prepared via the suggested process, i.e., the sequenced adding process in which SCMC is mixed with active powders prior to the addition of SBR, a much better electrochemical performance is obtained than that of the one prepared via the process referred as the simultaneous adding process, in which mixing of SCMC and SBR with active powders in simultaneous.

1. Introduction

Since lithium iron phosphate ($LiFePO_4$) is reported as a potential cathode-active material for lithium-ion batteries by Goodenough and his coworkers in 1997 [1], it has attracted considerable attention and has been extensively studied during the past decade. The advantages of the olivine $LiFePO_4$ are the large theoretical capacity [1], good cycle life performance [1,2], and safety [3—5]. The excellent structural stability of $LiFePO_4$, resulting from the strong Fe—P—O bonds, also greatly increases its thermal stability at high temperatures in its fully charged state [6—8]. In addition, the low cost and low toxicity of $LiFePO_4$ due to its environmentally compatible constituents make it a promising cathode-active material for large batteries [1,9]. Nevertheless, $LiFePO_4$ has some disadvantages such as poor electrical conductivity ($\sim 10^{-9}$ S cm^{-1}) and low diffusion of lithium ions (Li$^+$) in $LiFePO_4$ [10,11]. These

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issues result in capacity and rate capability losses, and thus hinder the commercial application of LiFePO$_4$. To enhance the electrical conductivity and ion diffusivity of LiFePO$_4$, surface coating by carbon [12–16] and reducing particle size [5,17,18] are two common approaches.

In addition to the physical and chemical properties of LiFePO$_4$ particles, good deagglomeration and dispersion of active powders (including LiFePO$_4$ and conductive agents) are also essential for obtaining reliable high-quality electrodes [19–24]. This is because powder agglomerates in an electrode will reduce the contact opportunity between them and this leads to poor electronic and ionic conduction. As a result, active powders and organic additives, such as polymeric binders and thickening agents, need to be homogeneously mixed in the solvent in the preliminary stage of the slurry preparation process. According to the type of solvent used, the as-prepared suspension can be classified into two categories: water-based (aqueous) and organic-based (nonaqueous) systems [25]. Because of environmental and cost considerations, water-based systems have attracted a lot of attention [9,26–31]. Nonetheless, these types of systems have the drawback of easy powder agglomeration [32], especially for carbon-related materials that are generally surface nonpolar and hydrophobic, and are unfavorable for wetting and dispersing in a water-based slurry. Since most commercial LiFePO$_4$ are surface-coated with carbon and typically use carbon materials as conductive agents, the dispersion of water-based LiFePO$_4$ electrodes is critical. To obtain well-dispersed LiFePO$_4$ electrode materials, two approaches of utilizing dispersants and changing the mixing sequence of the electrode materials have been proposed in the literature [19–24,33,34]. The efficient dispersants that have been proposed are isooctylphenyether of polyoxyethylene [19], poly(acrylic acid) (PAA) [20,21], poly(4-styrene sulfonic acid) (PSSA) [23], and poly(acrylic acid-*co*-maleic acid) [24]. The commonly suggested mixing sequence for manufacturing electrodes is adding the electrode materials in multiple steps rather than a single step [33,34].

Moreover, it has been known that styrene–butadiene rubber (SBR) and sodium carboxymethyl cellulose (SCMC) are ordinarily the binder and thickening agent for the water-based electrode, respectively [9,35–38], and SCMC is known to exhibit dispersion efficiency for graphite [37]. As a result, it can be inferred that SCMC may also disperse the active powders of LiFePO$_4$ electrodes, i.e., further addition of dispersant may not be required for the dispersion of water-based LiFePO$_4$ electrode when SCMC is used as the thickening agent. In this investigation, the procedure of mixing SCMC to obtain a well-dispersed LiFePO$_4$ electrode slurry is discussed by clarifying the interactions of organic additives and active powders based on studies of surface chemistry. It was found that the relative adding sequence of SCMC to SBR is important for the dispersion of LiFePO$_4$ electrode slurry because SBR is better than SCMC in interacting with and adsorbing on LiFePO$_4$, whereas only the adsorption of SCMC is effective for the deagglomeration and dispersion of LiFePO$_4$. In addition, the association between the preparation procedure of the electrode slurry, and the resulted dispersion and electrochemical properties of the electrode were also discussed.

2. Experimental

The cathode-active material used in this study was LiFePO$_4$ powder (Tatung Fine Chem. Co., Taiwan), which has a carbon content of 1.5 wt% and a median size of 130–140 nm as measured by the light-scattering (LA300, Horiba, Japan) method. Synthetic graphite (Timrex KS6, Timcal A+G Sins, Switzerland) with d$_{90}$ of 5.8–7.1 μm and carbon black (CB) (Super-P, Timcal A+G Sins, Switzerland) with an average size of 40 nm were used as

conductive agents. The binder used was SBR (Asahi Kasei Corporation, Japan) in the form of an aqueous emulsion of 48 wt% with a viscosity of 130 mPa s at 25 °C. The thickening agent used for SBR was SCMC (Aldrich, USA) having a molecular weight of 250,000 g mol^{-1} and a substitution degree (DS) of 1.2. The thickening agent was mixed with SBR in a weight ratio of 3:7. Deionized water was used as solvent.

Fig. 1 shows two procedures for preparing water-based LiFePO$_4$ slurries: the sequenced adding process denoted as the "SEQ process" and the simultaneous adding process denoted as the "SIM process." The slurries prepared with these two processes have the same ingredients, which are given in Table 1. For the SEQ process (Fig. 1(a)), the electrode slurry was prepared by premixing the active powders with an aqueous solution of SCMC under deagglomeration through ball milling for one day using Y$_2$O$_3$-stabilized ZrO$_2$ as the milling medium at room temperature. Then, SBR was added under continuous mixing and deagglomerating conditions for another three days. For the SIM process (Fig. 1(b)), SCMC and SBR were mixed together prior to adding the active powders, and then deagglomeration through ball milling was applied for four days after the active and conductive powders were added. The rheological properties of the as-prepared slurries were determined using a concentric cylinder rheometer (AR1000, TA Instruments
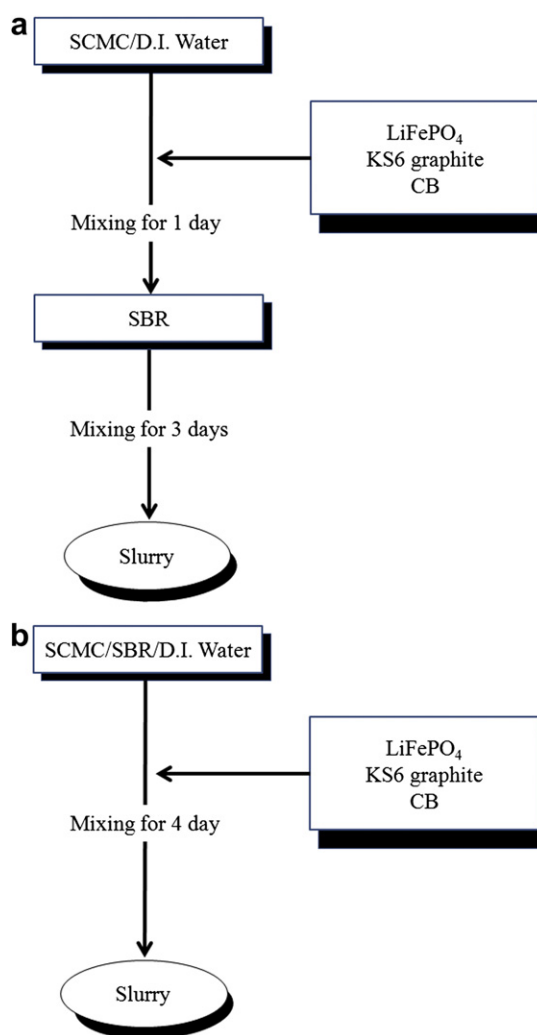

Fig. 1. Two procedures with (a) SEQ and (b) SIM processes for preparing water-based LiFePO$_4$ electrode slurries.

Table 1
Constituents for the LiFePO$_4$ electrode slurries and the corresponding dried electrode sheets.

Constituents	Contents (wt%)	
	Based upon wet slurry	Based upon dried sheet
Active powders:		
LiFePO$_4$	41.2	79.7
KS6 graphite	1.4	2.6
CB	4.1	7.9
Organic additives:		
SBR	1.5	2.9
SCMC	3.5	6.8
Solvent:		
D.I. water	48.3	–

Ltd., UK). Cone-plate geometry fixtures with a diameter of 20 mm and a cone angle of 1° were chosen for the steady shear rotation and dynamic frequency sweep tests. The relative viscosity is defined as the ratio of the apparent viscosity of the electrode slurry to that of the aqueous SCMC solution [39,40]. In dynamic measurements, the dynamic sweeps were carried out with an angular frequency (ω) varying from 0.6283 to 628.3 rad s^{-1} at a given strain in the linear viscoelastic regime. The surface chemistry of active powders in the absence and presence of SBR and SCMC was characterized by a technique known as the electro-acoustic method (ZetaProbe, Colloidal Dynamics Inc., USA). For measurements of zeta potentials, aqueous powder suspensions with solid loadings of 5 wt% LiFePO$_4$, 1 wt% KS6 graphite, and 1 wt% CB were used. The pH value of each powder suspension was adjusted by using aqueous solution of hydrochloric acid and sodium hydroxide during measurements of zeta potentials. In the sedimentation experiments, 10 wt% aqueous suspensions of LiFePO$_4$, KS6 graphite, and CB with and without SBR or SCMC were prepared and left in the graduated cylinders for seven days, and then the final sedimentation heights were recorded.

To prepare electrode sheets, the LiFePO$_4$ slurries were individually cast on one side of an aluminum (Al) foil by using a roller coater. The thickness of the electrode sheets was approximately 80 μm after drying at 80 °C. Each dried electrode sheet had to be further dried in a vacuum oven under a pressure of 10^{-3} Torr and a temperature of 100 °C for another 12 h before measuring the electrochemical properties. The microstructures of the electrode sheets were examined using a field emission scanning electron microscope (FESEM, S-470, Hitachi, Japan). In the compression experiment of the electrode sheets, a pressure of 7.5 tons cm^{-2} was applied. The electrochemical performance was evaluated by assembling 2016 cathode-limited lithium coin cells in an argon-filled glove box. LiFePO$_4$ was used as the cathode and a lithium metal foil electrode was used as the anode. A separator (Celgard 2320) was placed between the cathode and anode. The electrolyte was 1.0 M lithium hexafluorophosphate (LiPF$_6$, Ferro Corp., Cleveland, OH) in EC:PC:DEC (3:2:5 in volume) mixed solvents. The rate capability was tested by charging the cells to 4.0 V at a constant current of 0.2 C and then discharging to 2.5 V at 0.2 C. The cells were cycled at 0.2 C between 2.5 V and 4.0 V. Cyclic voltammograms (CV) of the cells were performed on a CHI 6081C workstation (American CH instrument) from 2.5 V to 4.0 V at a scanning rate of 0.5 mV s^{-1}.

3. Results and discussion

Fig. 2(a)–(c) shows the effect of adding organic additives, SBR and SCMC, on the surface chemistry of LiFePO$_4$, KS6 graphite, and CB, respectively. In Fig. 2(a), the isoelectric point (IEP) of LiFePO$_4$ is not shown, and its zeta potential is negative between −20 mV
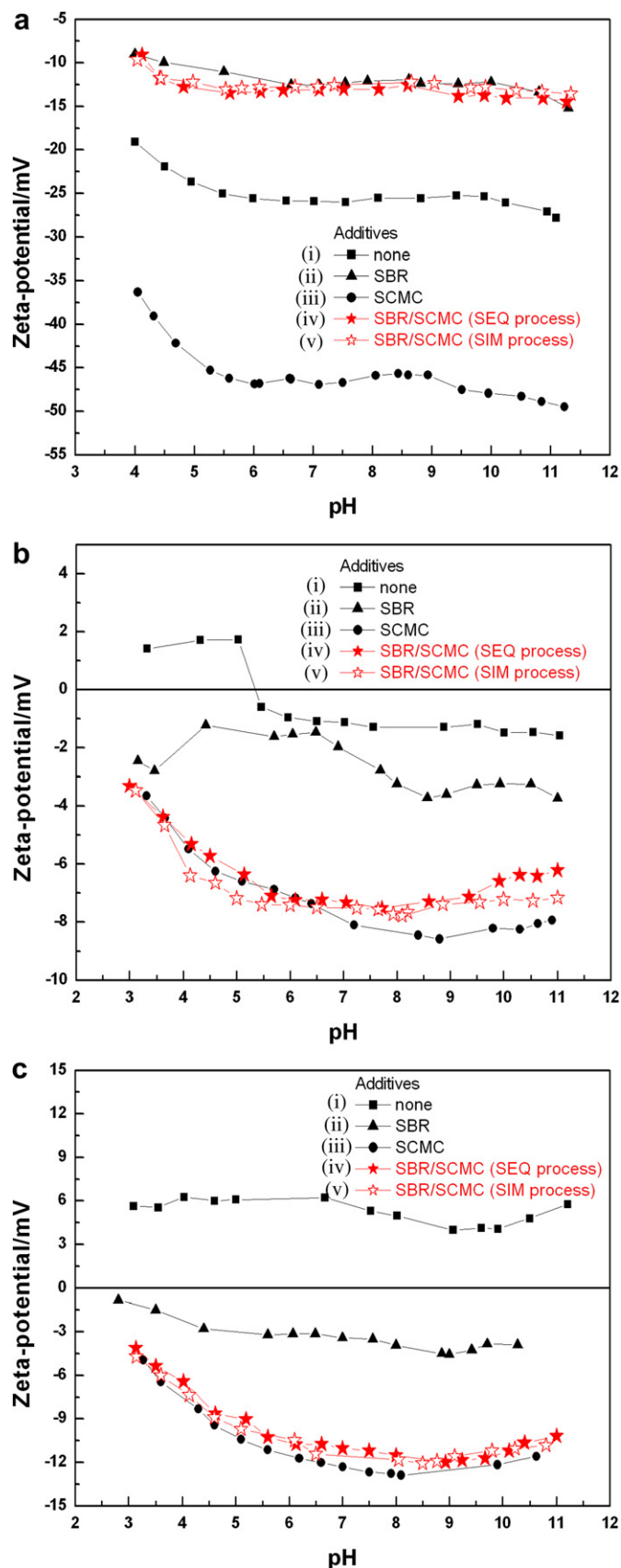

Fig. 2. Zeta potentials of (a) 5 wt% LiFePO$_4$, (b) 1 wt% KS6 graphite, and (c) 1 wt% CB in aqueous suspension in the (i) absence and presence of (ii) SBR, (iii) SCMC, (iv) SBR and SCMC added via the SEQ process, and (v) SBR and SCMC added via the SIM process.

and −28 mV in the pH range investigated. An upward shift of the zeta potential curve of LiFePO$_4$ was obtained when SBR was added, indicating that specific adsorption of SBR occurred on LiFePO$_4$. Note that specific adsorption is commonly due to strong interactions and not just weak van der Waals force between the adsorbate and adsorbent [39,40]. Because the chemical structure of SBR is deficient in polar functional groups, the specific adsorption of SBR only shields the surface charges and reduces the thickness of the electrical double layer around LiFePO$_4$ [39], and results in lower zeta potentials. In contrast, the addition of SCMC shifts the zeta potentials of LiFePO$_4$ to more negative values; this also demonstrates the occurrence of specific adsorption of SCMC on LiFePO$_4$. Because SCMC can dissociate to carry anionic charges, the specific adsorption of SCMC increases the negative charge density and the magnitude of the zeta potential of LiFePO$_4$.

From Fig. 2(b), it is obvious that KS6 graphite has an IEP at pH 5.3 and the magnitude of all its zeta potentials is low [23]. This is attributed to the nonpolar nature of KS6 graphite and its insignificant electrical double layer. With the addition of SBR and the disappearance of IEP, all the zeta potentials of KS6 graphite shift to values that are more negative. Thus, specific adsorption of SBR on the particle surface of KS6 graphite is suggested. Nevertheless, the slight increase in the negative values of zeta potentials cannot be caused by the adsorbed SBR because of its nonpolar chemistry, but it is possibly contributed by the anionically charged surfactant that resided on SBR during polymerization. A significant increase in negative potentials of KS6 graphite was observed with the addition of SCMC, which also reveals the occurrence of specific adsorption by SCMC. Fig. 2(c) shows the effect of adding SBR and SCMC on the surface chemistry of CB. The results are similar to those of Fig. 2(b), demonstrating the specific adsorption of both SBR and SCMC on CB.

To compare the efficiencies of the specific adsorption of SBR and SCMC in dispersing active powders, the sedimentation properties of the aqueous powder suspensions were explored. Fig. 3 shows the sedimentation of aqueous suspensions of LiFePO$_4$, KS6 graphite, and CB in the absence and presence of SBR or SCMC settled for seven days. Obviously, mixing with SBR reduces the sedimentation heights of LiFePO$_4$ (Fig. 3(a)-ii) and KS6 graphite (Fig. 3(b)-ii) from 2.6 cm to 1.0 cm and from 5.6 cm to 0.6 cm, respectively, indicating that SBR has some efficiency in dispersing these two powders. When mixing with SCMC, the dispersion stability of the powder suspensions of LiFePO$_4$ and KS6 graphite is excellent, and both of them are difficult to settle completely and show an indistinct interface between the upper supernatant and settled powder. These results indicate that SCMC is highly efficient in dispersing these two powders. The sedimentation of CB is shown in Fig. 3(c); CB is originally well-suspended with negligible sediment. This is attributed to its small particle size of 40 nm. With the addition of SBR, CB remains as before; moreover no sediment was observed when SCMC was added. Based on the above observations, it can be concluded that both SBR and SCMC are efficient in dispersing active powders, but the efficiency of SBR is much lower than that of SCMC. Because SBR does not significantly increase the magnitude of the zeta potentials of active powders, the dispersion mechanism for the addition of SBR should primarily belong to the steric stabilization effect [39,40]. Nevertheless, SCMC is a dissociable polyelectrolyte and hence its specific adsorption provides active powders with steric hindrance and electrostatic repulsion simultaneously, i.e., the dispersion mechanism for the addition of SCMC primarily belongs to the electrosteric stabilization effect [39,40].

Because SBR and SCMC can interact with active powders to specifically adsorb on them (Fig. 2), it will be important to further clarify whether a competitive adsorption occurred between SBR
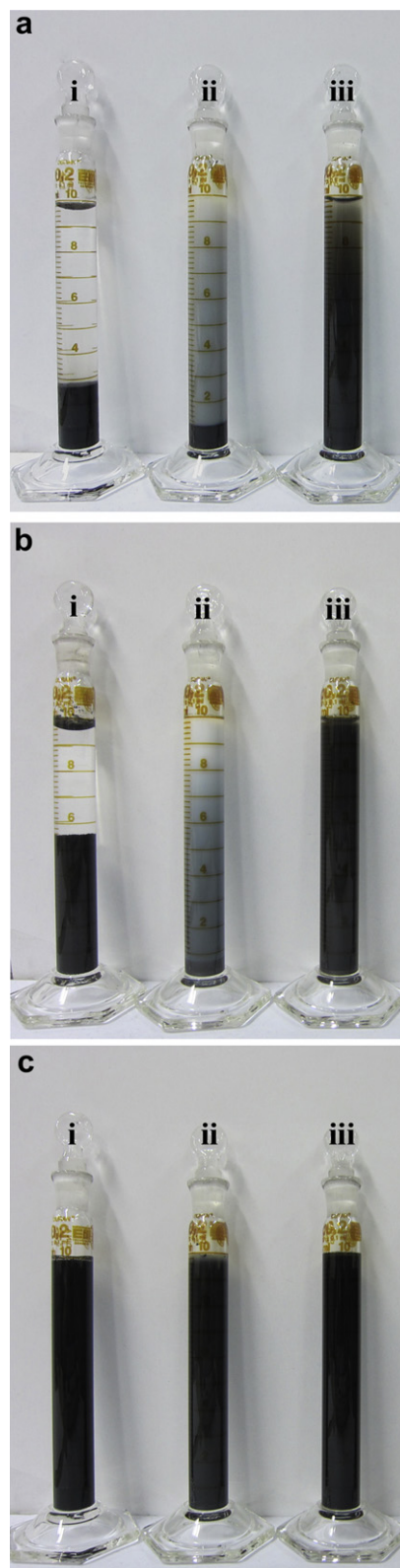

Fig. 3. Pictures showing graduates containing 10 wt% aqueous suspensions of (a) LiFePO$_4$, (b) KS6 graphite, and (c) CB in the (i) absence and presence of (ii) SBR or (iii) SCMC.

and SCMC, and its effect on the dispersion properties of active powders. The zeta potentials of active powders in the presence of SBR and SCMC added in different sequences were further studied. As shown in Fig. 2, the data denoted by closed stars (★) represent the zeta potentials of the active powder that was mixed with SCMC and SBR following the SEQ process of Fig. 1, i.e., SCMC was added into the aqueous powder suspension prior to SBR, whereas the data denoted by open stars (☆) represent those obtained by the SIM process. Fig. 2(a) shows that both the zeta potential curves of LiFePO$_4$ with additions of SCMC and SBR almost overlap with that of only adding SBR regardless of the mixing process. This result demonstrates higher priority and greater competition of the adsorption of SBR than that of SCMC, i.e., the adsorption of pre-added SCMC via the SEQ process will be replaced by the adsorption of latter-added SBR. Furthermore, the adsorption of co-added SCMC via the SIM process will be difficult to happen because of the strong competition of SBR. However, the result "eventually adsorbed by the more competitive SBR" does not mean that the dispersion properties of the two LiFePO$_4$ suspensions prepared via the SEQ and SIM processes will be the same. According to the dispersion mechanism shown in Scheme 1(a), LiFePO$_4$ can be efficiently deagglomerated owing to the electrosteric effect caused

by the adsorbed SCMC before the addition of SBR when the SEQ process is performed. Note that even in the case of the latter-added SBR that replaces the SCMC, LiFePO$_4$ has already been deagglomerated. In addition, SBR still exhibits slight dispersion efficiency and thus when replaced, LiFePO$_4$ should not reagglomerate. For the suspension prepared via the SIM process, only the adsorption of SBR is possible for LiFePO$_4$ because of its greater competition. However, the dispersion efficiency caused by the steric effect from the adsorbed SBR is insufficient, and thus heavy agglomerates of LiFePO$_4$ remained in the aqueous suspensions can be expected.

The effect of competitive adsorption between SBR and SCMC on the zeta potentials of KS6 graphite is shown in Fig. 2(b). By adding SBR and SCMC via the SEQ or SIM process, both the zeta potential curves of KS6 graphite overlap with that observed by adding only SCMC. This result is just the opposite of that occurred on LiFePO$_4$, and indicates that SCMC is more competitive than SBR in adsorbing on KS6 graphite. Scheme 1(b) proposed the dispersion mechanisms of KS6 graphite in the presence of SBR and SCMC mixed via the SEQ and SIM processes. By the SEQ process, KS6 graphite is well dispersed due to the electrosteric effect caused by the first-added SCMC, whereas the latter-added SBR does not affect the adsorption of SCMC. According to the SIM process, KS6 graphite can also be well dispersed because SCMC has a higher priority to adsorb and results in better dispersion efficiency (Fig. 3(b)). A similar result was observed in the competitive adsorption of SBR and SCMC on CB (Fig. 2(c)), i.e., SCMC is also more competitive than SBR in adsorbing on CB. Based on these results, it is shown that the relative adding sequence of SBR and SCMC is particularly important for the dispersion of LiFePO$_4$, because SBR preferentially adsorbs LiFePO$_4$ and this does not facilitate its dispersion. However, LiFePO$_4$ is the primary powder with the largest volume in an electrode, and its dispersion determines the dispersion of the as-prepared slurry. Therefore, to have a better dispersed electrode slurry, we suggest mixing SCMC with active powders prior to the addition of SBR.

To verify the importance of the prior addition of SCMC on the dispersion of the electrode slurry, the rheologies of the aqueous electrode slurries prepared via the SEQ and SIM processes were compared. To understand the flow behavior of the active powders and their exact dispersion properties in a slurry, we show the relative viscosities of the electrode slurries as a function of shear rate in Fig. 4(a), in which the rheological contribution from SCMC that commonly exhibits a strong intrinsic shear-thinning property has been excluded [9]. It was found that both slurries have a complex rheology in the presences of shear-thickening at low shear rate and shear-thinning at high shear rate. The exhibition of shear-thickening behavior suggests that the active powders in both slurries are agglomerated, but the agglomeration of the powders is lower for the slurry prepared via the SEQ process, which was revealed from its lower relative viscosity. Furthermore, the interactions of active powders and the dispersion structures of the two slurries were identified by measuring their viscoelastic properties. Fig. 4(b) shows the frequency dependence of the storage (G′) and loss (G″) moduli for these two slurries. It is obvious that the values of G′ for these two slurries are higher than those of G″, indicating that both have a more solid-like (or network) structure than a liquid-like (or dispersed) structure. Therefore, both of them are strictly not well dispersed, although the dispersion of the slurry prepared via the SEQ process is relatively better than that prepared via the SIM process. The relatively better dispersion of the SEQ-processed slurry can also be evidenced by its shorter characteristic relaxation times (τ_c). τ_c is the reciprocal of the crossover frequency (ω_c) that is related to the crossover point (COP) where
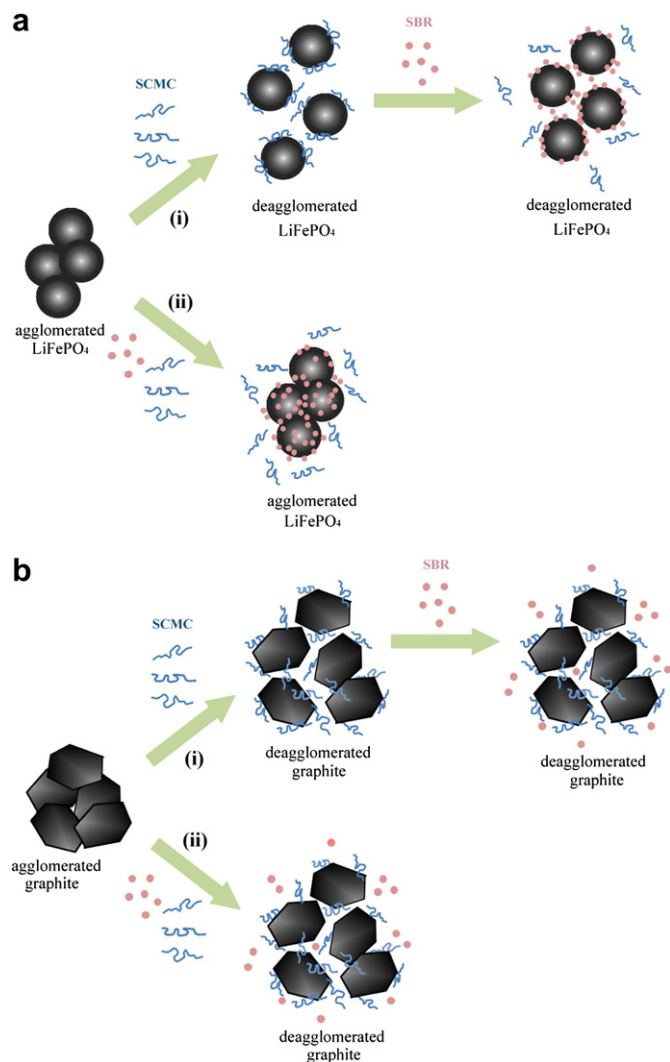
Scheme 1. Diagrams showing dispersion mechanisms of (a) LiFePO$_4$ and (b) KS6 graphite in an aqueous suspension with the presence of SBR and SCMC added via the sequence of (i) SEQ and (ii) SIM process.
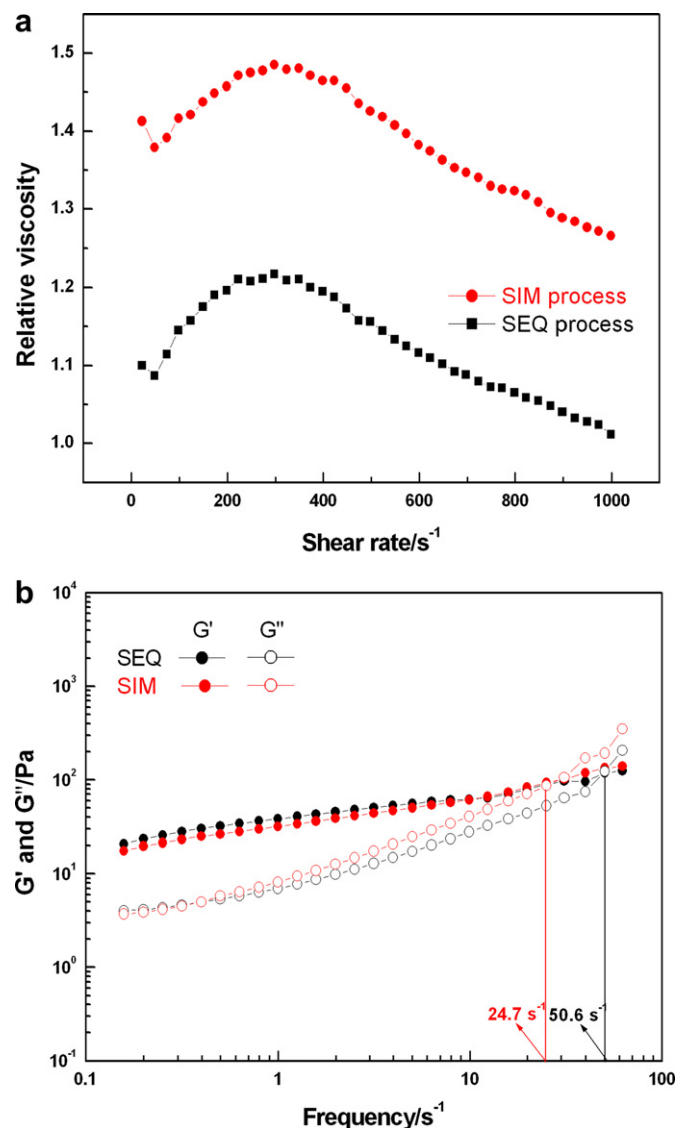
Fig. 4. (a) Relative viscosity as a function of shear rate and (b) G′ and G″ as a function of the sweeping frequency for 41.2 wt% LiFePO$_4$ electrode slurries prepared via the SEQ and SIM processes.

Fig. 5. SEM micrographs of the top surfaces of LiFePO$_4$ electrode sheets prepared via the (a) SIM and (b) SEQ processes.

electrode sheet are more agglomerated, they will be less compact to have a lower relative density and higher porosity. Table 2 lists the relative densities and porosities of the SEQ- and SIM-processed electrode sheets with/without being compressed. Note that the relative densities of these two electrodes are under 35% before compression, which low densities are because both electrodes have a low solid loading of cathode powders (Table 1). Nevertheless, it is still clear that the SEQ-processed electrode sheet has higher relative densities and lower porosities than the SIM-processed electrode, evidencing the relatively better dispersion efficiency of the SEQ process.

Based on the above results, it is shown that the interaction and adsorption priorities of the organic additives have great impact on the determination of mixing procedure for preparing the electrode slurry; furthermore, a different procedure will result in different dispersion properties. To clarify how the preparation procedure as well as the dispersion of the slurry affects the electrochemical properties of the as-cast electrodes, the cyclic voltammograms of the LiFePO$_4$ electrodes prepared via the SEQ and SIM processes were measured and compared in Fig. 6. For the uncompressed electrodes (solid lines), the oxidation and reduction peaks of the electrode prepared via the SEQ process are more symmetrical and sharper with a higher intensity than those of the other electrode. Moreover, the electrode prepared via the SEQ process exhibits less difference in potentials between its oxidation and reduction peaks, i.e., 0.441 V, than that via the SIM process, which is 0.608 V. This is probably because the active powders in the SEQ-processed LiFePO$_4$ electrode have been more deagglomerated and their

the G′ and G″ are equal [40–42]. For a slurry having a lower ω_c or a longer τ_c, a poorer dispersion is suggested, whereas a higher ω_c or a shorter τ_c associates to a slurry having a better dispersion. As shown in Fig. 4(b), the G′ and G″ for the slurry prepared via the SEQ process cross at a ω_c of 50.6 s^{-1} that is significantly higher than 24.7 s^{-1} of the SIM-processed slurry.

Fig. 5 shows the microstructures of the top surfaces of the as-cast LiFePO$_4$ electrode sheets prepared via the SIM and SEQ processes, in which the insets are the images with lower magnification. For the SIM-processed electrode sheet (Fig. 5(a)), the cathode powders show heavily agglomerated and the sheet surface is coarse, demonstrating the poor dispersion and inhomogeneous distribution of cathode materials. For the SEQ-processed electrode sheet (Fig. 5(b)), the agglomerated size of the cathode powders is significantly smaller, and the sheet surface is smoother and denser. In addition to the analyses of rheology and SEM, the dispersion efficiencies of processes were also assessed quantitatively by measuring the relative density and porosity of the electrode sheets. When powders in the cast
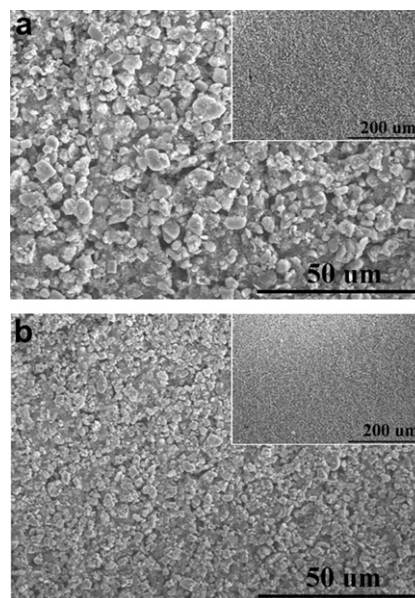
Table 2
The relative densities and porosities of the SEQ- and SIM-processed electrode sheets with/without being compressed.

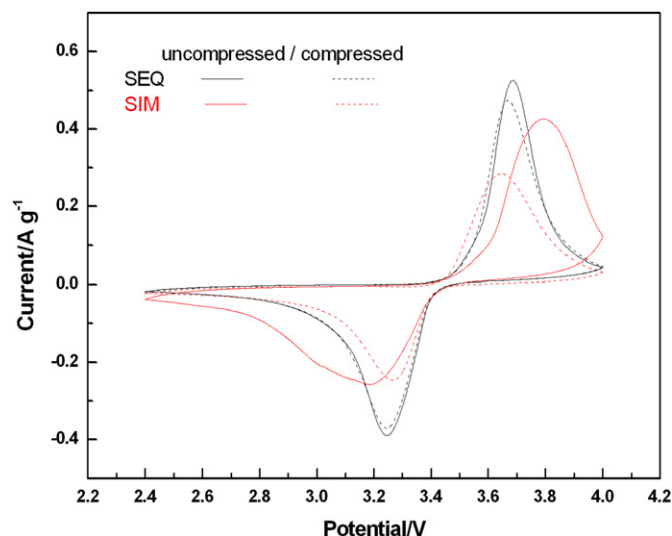| Preparation process	Relative density (%)		Porosity (%)	
	Uncompressed	Compressed	Uncompressed	Compressed
SEQ	35.0	65.1	65.0	34.9
SIM	30.2	61.5	69.8	38.5

Fig. 6. Cyclic voltammograms of cells constructed with uncompressed (solid lines) and compressed (dashed lines) LiFePO$_4$ electrodes prepared via the SEQ and SIM processes.

Fig. 7. Discharge curves at discharge rates of 0.2 C, 1 C and 3 C for cells constructed with (a) uncompressed and (b) compressed LiFePO$_4$ electrodes prepared via SEQ and SIM processes.

smaller particle size provides less diffusion lengths for Li$^+$. In addition, the greater deagglomeration of the active powders in the electrode can cause better kinetics for the intercalation and deintercalation of Li$^+$ and more reversible electrochemical reactions. Based on the results of the compressed electrodes, the process of compression shows insignificant influence on the current peaks of the electrode prepared via the SEQ process. This is probably because of the fact that the active powders in the SEQ-processed electrode have better contacts and thus further compression is not that helpful [43]. Instead, compression improves the peak symmetry and changes the peak intensities for the SIM-processed electrode. It has been known that there are more agglomerates in the SIM-processed electrode; hence, some of them might be able to be further broken up by the compression force, which shortens the diffusion length and improves the contact between active powders and kinetics for the intercalation and deintercalation of Li$^+$.

The effect of the preparation procedures of electrode slurries on the electrochemical properties of electrodes was also revealed in the rate capability and the cycle life performances. Fig. 7 shows the discharge curves at 0.2 C, 1 C and 3 C for the cells constructed with uncompressed and compressed SEQ- and SIM-processed LiFePO$_4$ electrodes. Without compression, the cell with the SIM-processed electrode has lower capacities and plateau voltages than that with the SEQ-processed electrode. Compared to the previous results of dispersion, the lower plateau voltage for the SIM-processed electrode is attributed to the higher resistance of the electrode sheet, i.e., the poorer the dispersion and the contact of cathode powders in an electrode, the larger the IR-drop. With compression, the cell with SEQ-processed electrode has slight improvement in its specific discharge capacity at 3 C, representing the reduction of the internal resistance. Moreover, it is found that compression makes the distortions of the discharge curves at 1 C and 3 C for the cell with the SIM-processed electrode insignificant. These results should be due to the cause of more approximate porosities attained by compression, which facilitates the contacts of cathode powders and improves the electrochemical properties.

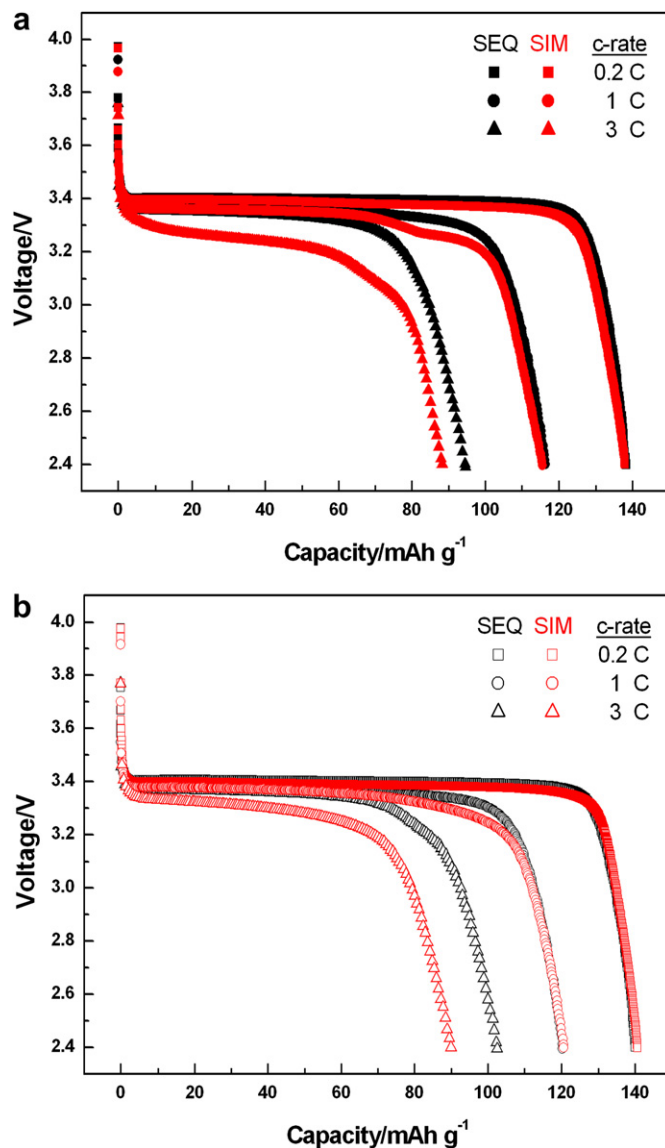Fig. 8 compares the cyclibilities of the two electrodes with/without being compressed. In the case of the electrodes that were not compressed, the cell constructed with LiFePO$_4$ electrode via the SEQ process displays good charge/discharge cyclability and shows a much better capacity retention of 90% than that of 25% shown by the cell constructed with the other electrode after the 100-cycles test. This can be realized owing to the better dispersion of the SEQ-processed electrode. With compression, good charge/discharge cyclability and a capacity retention of 90% remain in the cell with the SEQ-processed electrode. However, great improvements in cyclability and capacity retention were observed in the cell with the SIM-processed electrode, although they are still poorer than those of the SEQ-processed electrode. It is believed that the maintenance of cyclability in the electrode via the SEQ process is owing to the smaller effect of compression on the deagglomeration and contacts of active powders; furthermore, the great influence of compression on the electrochemical performances of the SIM-processed electrode should be caused by a further breakdown of larger agglomerates in the electrode.
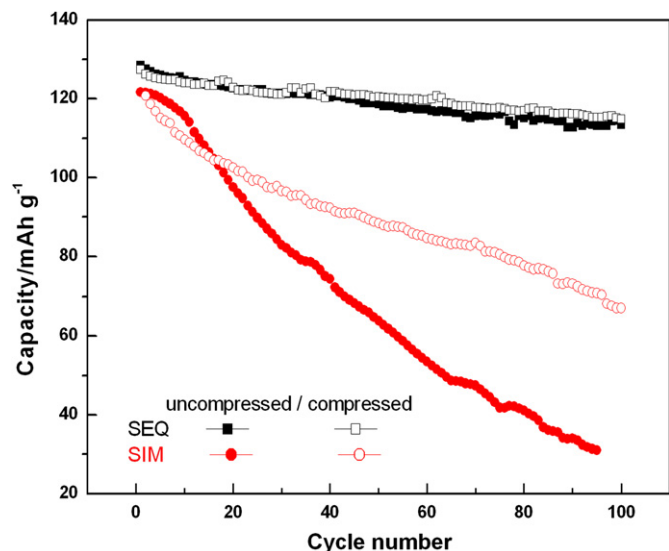
Fig. 8. Cycling stability of cells constructed with uncompressed and compressed LiFePO$_4$ electrodes prepared via the SEQ and SIM processes.

4. Conclusions

In this study, we discussed the effects of the interactions between active powders and organic additives on the dispersion and electrochemical properties of LiFePO$_4$ electrodes. Based on the results of zeta potential and sedimentation measurements, it is concluded that both organic additives, SBR and SCMC, can interact with and adsorb on active powders of LiFePO$_4$, KS6 graphite, and CB. Because SBR is chemically nonpolar, its adsorption primarily provides steric hindrance to the dispersion of active powders, which is referred to as the steric stabilization effect. Nevertheless, the adsorption of SBR does not effectively disperse active powders. SCMC, however, is a dissociable poly-electrolyte, and its adsorption causes active powders to simultaneously exhibit steric and electrostatic repulsions, which is referred to as the electrosteric stabilization effect that is effective for the dispersion of active powders. In the studies of competitive adsorption between SBR and SCMC on active powders, it was found that LiFePO$_4$ preferentially interacts with SBR than with SCMC, resulting in a higher priority for SBR to adsorb and dominate the surface chemistry. In contrast, the conductive agents, KS6 graphite and CB, prefer to interact with SCMC and result in a higher priority for the adsorption of SCMC. Based on the considerations of the interaction priority and the dispersion efficiency of organic additives, a mixing procedure that facilitates the preparation of a better dispersed electrode slurry was suggested, which is referred to as the SEQ process. By the SEQ process, LiFePO$_4$ and conductive agents are more deagglomerated and dispersed by the pre-added SCMC. For comparison, another procedure that simultaneously mixes SBR and SCMC with active powders was also carried out, which is referred to as the SIM process. By the SIM process, LiFePO$_4$ is more difficult to be deagglomerated because SCMC hardly competes with the co-added SBR to adsorb on and disperse LiFePO$_4$. Moreover, the different dispersion properties due to the use of different preparation procedures were also demonstrated by the rheologies of the slurries. The slurry prepared via the SEQ process exhibits a higher ω_c, demonstrating a more liquid-like dispersion structure with better fluidity. The lower ω_c obtained from the slurry prepared via the SIM process demonstrates a more solid-like (network) structure with poorer fluidity. In addition, the SEQ-

processed LiFePO$_4$ electrode shows better performance on the cyclic voltammograms, rate capability and cyclability of its constructed cell, verifying that it has better kinetics for Li$^+$ diffusion as well as better intercalation and deintercalation because of the more deagglomerated active powders. For the electrode via the SIM process, a poorer electrochemical performance was obtained. This reveals poorer kinetics of Li$^+$ in this electrode, which can be improved by the additional process of compression that is believed to be able to further break up the powder agglomerates. In conclusion, to design an approximate process for the preparation of a better dispersed electrode slurry with good electrochemical performance, clarifying the interactions of organic additives with active powders is the prerequisite.

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